Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Applied Science Research, 2013, 5 (2):208-212
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Study of optical, thermal and mechanical properties of trisglycine zinc chloride: A semiorganic non-linear optical single crystal

J. Uma* and V. Rajendran

Department of Physics, Presidency College, Chennai

ABSTRACT

Single crystals of semi organic material Trisglycine zinc chloride (TGZC) were grown from aqueous solution by slow evaporation solution growth technique. Single crystal X-ray Diffraction analysis was used to estimate the cell parameters of the grown crystals. The grown crystals were tested by FTIR, thermo gravimetric and differential thermal analysis and UV–vis–NIR analysis. The absorbance spectrum of TGZC crystal is used to calculate the band gap and it is found to be 4.93eV. The second harmonic conversion efficiency of TGZC was determined using the Kurtz and Perry powder technique. It was observed to be 0.5 times greater than that of KDP. The mechanical strength of the crystal is determined by Vicker's Hardness test.

Keywords: Single crystal growth, X-Ray Diffraction, NLO material, FTIR, optical studies, thermal analysis.

INTRODUCTION

The synthesis of novel and efficient frequency conversion materials has resulted in the development of semi-organic materials, which possess large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical stability [1–3]. Amino acids are interesting organic materials for NLO applications as they contain zwitterions, which create hydrogen bonds. Amino acids have two or more types of coordination atoms and can act as various bridging ligands[4,5]. Glycine is the simplest amino acid. Some complexes of Glycine with inorganic salts are Lithium Sulphate[6], Sodium Nitrate[7], Potassium Sulphate[8], and Zinc Chloride[9] that forms NLO semiorganic crystals. Hariharan et al. [10] and Fleck et al.[11] have studied the crystal structure and phase matching studies on Trisglycine Zinc Chloride. Wojciechowski et al.[12] have studied laser induced optical effects of Trisglycine Zinc Chloride. The present paper deals with the growth of Trisglycine Zinc Chloride (TGZC) by slow evaporation solution growth technique and characterization by single-crystal X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectrum, UV analysis, NLO and microhardness test.

MATERIALS AND METHODS

MATERIAL SYNTHESIS

Trisglycine Zinc Chloride (TGZC) was synthesized by dissolving high purity Glycine and Zinc Chloride in the ratio of 3:1 in deionised water with continuous stirring. The prepared solution was left for evaporation at room temperature and crystals were obtained within a period of 20 days. The impurity content of TGZC was minimized by recrystallization process. The grown crystals were optically transparent and are shown in Figure 1.

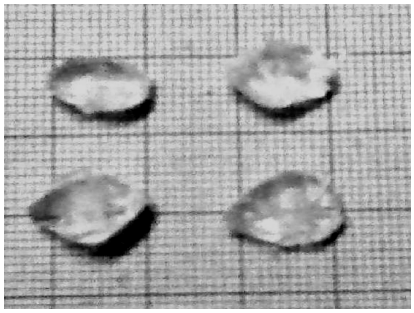

Fig 1. As grown crystal of TGZC by slow evaporation technique.

RESULTS AND DISCUSSION

3.1. Single Crystal X-Ray Diffraction analysis

Single-crystal X-Ray Diffraction analysis for the grown TGZC crystal has been carried out using Bruker Kappa APEX-II Diffractometer. The determined lattice parameters a=11.20 Å, b=15.19 Å, c=15.54 Å and volume =2642 $Å^3$ are in good agreement with the reported values [10]. TGZC belongs to orthorhombic system with space group $Pbn2_1$, which is recognized as noncentrosymmetric, thus satisfying the basic and essential material requirements for the SHG activity.

3.2. FTIR Spectral Analysis

The FTIR spectrum was recorded using a Perkin–Elmer FTIR spectrum RXI spectrometer by KBr pellet technique in the range 450–4000 cm^{-1} at room temperature. The FTIR spectrum is shown in Figure 2.Glycine exists as zwitterions in the crystalline state both in free molecule and in sandwich complex. The $–CH_2$ group frequencies are not affected since they are not metal sensitive. The broad peak at 3180 cm^{-1} is considered to be due to the $–NH_2$ group. The broadness of the peak in the region of 2800–3400cm^{-1} is due to intermolecular hydrogen bonding existing between the two layers of Glycine of Dichlorodiglycinezinc (II) and Glycine molecule [13]. CCN stretching is revealed by the peak at 1032cm^{-1}. Strong bands traced at 917 and 1324cm^{-1} are due to the C–H stretching mode vibrations. The peaks observed at 1641, 1411, 672 and 592cm^{-1} indicate the presence of Carboxylate group. The transmission due to the Carboxylate group of free Glycine is observed at 1610, 1413, 694 and 607cm^{-1} [14]. Similarly the absorption peaks due to the NH_3^+ group of free Glycine at 3175, 1492,1131 and 516$cm^{-1}$are shifted to 3180, 1499, 1134 and 513cm^{-1}respectively. The link between the molecules in each layer is through hydrogen bonds. The two layers are also interlinked by hydrogen bonds [10].

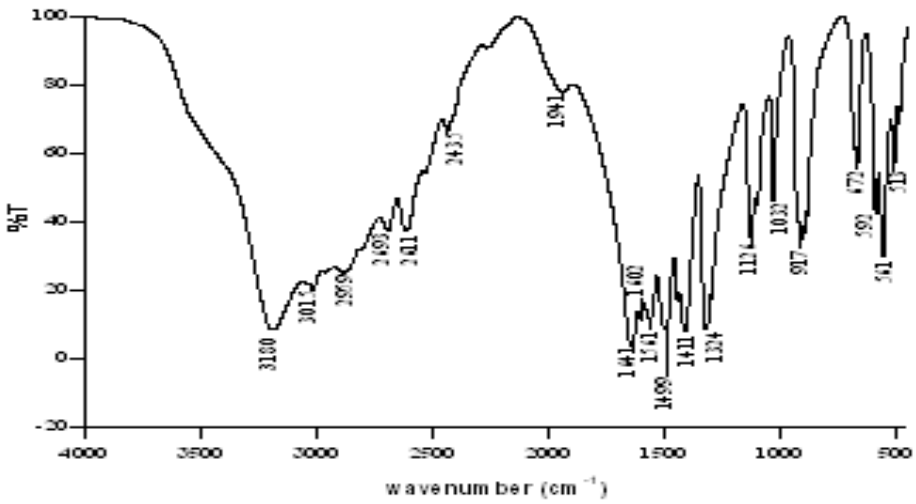

Fig. 2.FT IR Spectrum of TGZC

3.3. Optical Studies

The optical absorption spectrum of the grown crystal was recorded in the wavelength range 200–2000nm using a Varian Cary 5e spectrophotometer. The absorption spectrum is shown in Figure 3. It is observed that the absorption is low in the entire visible and near infrared region with the lower cut-off wavelength at 250nm.It suggests that the

material is quite suitable for SHG studies and other related optoelectronic applications [15]. The dependence of optical absorption coefficient on photon energy helps to study the band structure and the type of transition of electrons [16]. The optical absorption coefficient (α) was calculated using the following relation

$$\alpha = \left(\frac{2.303}{t}\right)\log\left(\frac{1}{T}\right)$$

where T is the transmittance and t is the thickness of the crystaland log (1/T) is defined as absorbance of the sample[17]. Optical band gap (Eg) was evaluated from the transmission spectra and optical absorption coefficient (α) near the absorption edge is given by [18].

$$(h\upsilon\alpha) = A\left(h\upsilon - E_g^{opt}\right)^{\frac{1}{2}}$$

where A is a constant, Eg the optical band gap, h the Planck constant and υ the frequency of the incident photons. The direct band gap of TGZC crystal was estimated by plotting $(\alpha h\upsilon)^2$ versus hυ as shown in Figure 4 and extrapolating the linear portion near the onset of absorption edge to the energy axis[19]. From the figure, the value of band gap was found to be 4.93eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [20].

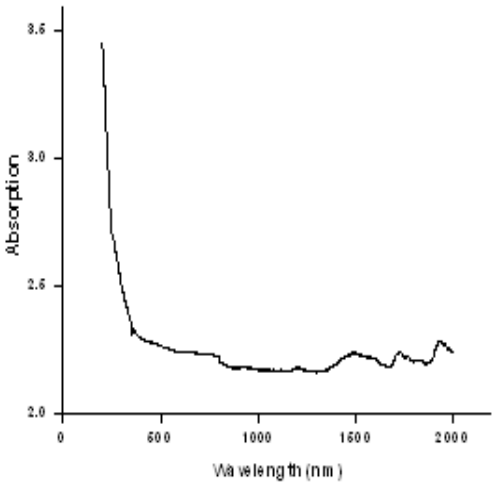

Fig. 3. Absorption spectrum of TGZC crystal

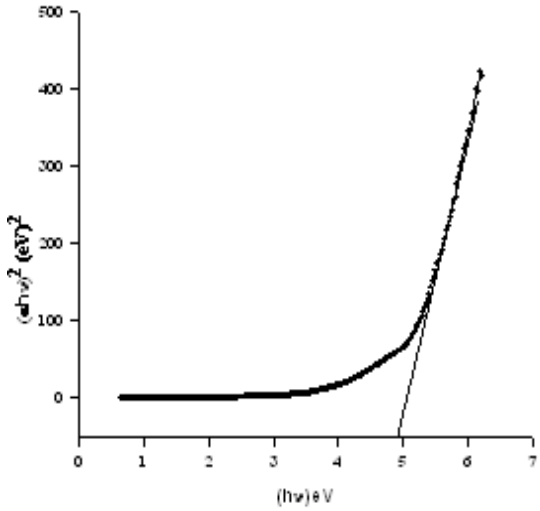

Fig.4. Band gap spectra of TGZC crystal

3.4. Second Harmonic Generation

The Second Harmonic Generation signal in TGZC crystals were examined by the Kurtz powder technique [21]. The fundamental beam of high-intensity (λ=1064 nm) from Q- switched Nd:YAG laser with pulse duration of 8ns with 10 Hz pulse rate was made to fall normally on the powdered sample cell. The Second Harmonic Generation behavior was confirmed from the emission of green light (λ=532 nm) and collected after separating the 1064 nm pump beam with an IR-blocking filter. SHG efficiency of the grown single crystal is 0.5 times that of the standard KDP crystal.

3.5. Thermal Analysis

Thermo Gravimetric analysis of the crystal was carried out in the temperature range 20–1300^{o}C in nitrogen atmosphere at the heating rate of 10^{o}C/min using the instrument NETZSCH STA 409C/CD thermal analyzer. The TGA–DTA curves of TGZC are illustrated in Figure 5. The curve shows an endothermic peak at 235^{o}C which can be attributed to the melting point of the sample. The study reveals that the initial decomposition of the sample starts at 235^{o}C and a weight loss of 39% observed between 235 and 420^{o}C. This is due to the loss of four Chlorine atoms attached to Zinc and two Glycine molecules, which are attached with Dichlorodiglycinezinc(II) by weak hydrogen bonding[13]. Beyond 420^{o}C, there is a weight loss of 52% due to the removal of remaining compounds attached with Zinc by coordinate bond. The results confirm that the crystal is stable upto 235 ^{o}C. Further, the compound has no phase transition till the material reaches the melting point, which enhances the temperature range of the crystal for NLO applications [22].

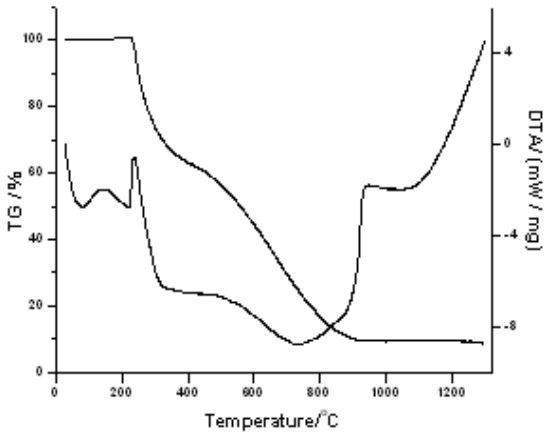

Fig .5. TG/DTA Curve for TGZC crystal

3.6. Microhardness Test

Hardness is a measure of the resistance to plastic deformation [23]. The hardness of the crystal carries information about the strength, molecular bindings, yield strength and elastic constants of the material. The mechanical property of the TGZC crystals was studied using SHIMADZU HMV 2T Vickers hardness tester, fitted with a Vickers's diamond pyramidal indenter.

The hardness values were calculated from the formula

$$Hv = \frac{1.8544\mathrm{P}}{d^2}$$

where P is the applied load and d is the mean diagonal length of the indentation. The trace is shown in Fig. 6, which shows that the hardness increases with the increase of load due to the release of internal stress generated by indentation [24]. The phenomenon of dependence of microhardness of a solid on the applied load, at low level of testing load is known as indentation size effect (ISE). Meyer's law [25] relates load and size of indentation as $P = ad^n$ connecting the applied load (P) and diagonal length (d) of the indentation, work hardening coefficient /Meyer's index 'n' was calculated. Here, 'a' is the constant for a given material. The work hardening coefficient was found to be 2.68 by taking a slope in the straight line of the graph drawn between logP and logd. Hv should increase with the increase of P if n>2 and decrease if n<2. According to Onitsch [26] and Hanneman [27] 'n' should lie between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials. The 'n' value observed in the present studies is around 2.68 suggesting that the grown TGZC crystal belongs to softer material category.The elastic stiffness constant (C_{11}) for different loads calculated using Wooster's empirical formula [28] $C_{11}=Hv^{7/4}$ are shown in

Table 1 which gives an idea about the tightness of bonding between neighboring atoms.

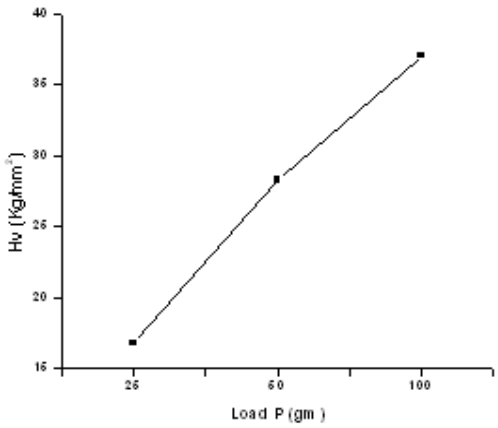

Fig. 6. Vickers hardness number vs. load

Table 1: C_{11} for various loads

S.No	Load (gm)	C_{11} ($x10^{12}$ Pa)
1	25	4.38557
2	50	10.9467
3	100	17.5531

CONCLUSION

A semiorganic NLO material Trisglycine Zinc Chloride (TGZC) was synthesized and single crystals have been grown by slow evaporation technique. From the single crystal X-Ray Diffraction analysis, lattice parameters were estimated. Functional groups and hydrogen environment were confirmed by FTIR analysis. The low optical absorption in the entire visible, near infrared region and lower cut-off wavelength facilitate it to be a potential material for NLO applications. The direct band gap energy for the grown crystal is found to be 4.93eV. Thermal analysis indicated that the grown crystal is stable up to 235 ^{o}C. The NLO behavior of the TGZC was confirmed by the Kurtz–Perry powder SHG technique. Microhardness study on TGZC crystals reveals that the Vickers hardness number Hv increases with increase in load and it belongs to soft material category as Meyer's index number ‘n’ is greater than 2.The stiffness constant C_{11} is quite high, revealing that the binding forces between the ions are quite strong. The above characterization and the nonlinear optical properties confirm that the grown crystal is suitable for the fabrication of various optoelectronic devices.

REFERENCES

[1] Y.R. Shen, *The Principles of Nonlinear Optics*, Wiley, New York, **1984**.
[2] H.O. Marcy, L.F. Warren, M.S. Webb, C.A. Ebbers, S.P. Velsko, G.C. Kennedy, *Appl. Opt.*,**1992**, 31, 5051 - 5060.
[3] S. Ledoux, J. Zyss, *J. Int., Nonlinear Opt. Phys.*,**1994**,3, 287-316.
[4] Y. Yukawa, Y. Inomata, T. Takeuchi, *Bull. Chem. Soc. Jpn.*,**1983**, 56, 2125-2128.
[5] Y.Yukawa, N.Yasukawa,Y.Inomata,T.Takeuchi, *Bull.Chem.Soc. Jpn*., **1985,**58,1591-1592.
[6] T. Balakrishnan, K. Ramamurthi, *Cryst. Res. Technol*.,**2006**, 41, 1184-1188.
[7] M. Narayan Bhat, S.M. Dharmaprakash, *J. Cryst Growth*.,**2002**, 235, 511-516.
[8] Ra. Shanmugavadivu, G. Ravi, A. Nixon Azariah, *J. Phys. Chem. Solids*.,**2006**, 67, 1858-1861.
[9] T. Balakrishnan, K. Ramamurthi, *Mater. Lett*.,**2008**, 62, 65-68.
[10] M. Hariharan, S.S. Rajan, R. Srinivasan, S. Natarajan, *Z. Kristallogr*.,**1989**,188,217-222.
[11] M. Fleck, P. Becker, L. Bayarjargal, R. Ochrombel, L. Bohaty´ , *Cryst. Res. Technol*., **2008**, 43, 127-134.
[12] Wojciechowski, I.V. Kityk, G. Lakshminarayana, I. Fuks-Janczarek, J. Berdowski, E. Berdowska Z. Tylczyn´ ski, Physica B: *Condens. Matter*.,**2010**, 405, 2827-2930.
[13]K.Sugandhi, S.Dinakaran, M.Jose, R.Uthrakumar, A.JeyaRejendran, G.Bhagvannarayana, V.Joseph,S.Jerome Das , *Physica B*.,**2010**, 405, 18, 3929-3935.
[14]K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, third Edn., John Wiley & sons Inc.*, **1978**.
[15] K.V. Rajendran, D. Jayaraman, R. Jayavel, R. Mohan Kumar, P. Ramasamy, *J. Cryst. Growth.*, **2001**, 224, 122-127.
[16] T.N. Ciupinaa,V. Prodana,G. Rusub,G.I. heorghies,C.Vasilec, *J.Opto electron Adv. Mater*.,**1967**,6, 211.
[17] V. Rajendran and S. Gnanam,*Der Pharma Chemica*, **2011**, 3, 6,606-613.
[18] A. Ashour, N. El-Kadry, S.A. Mahmoud, *Thin Solid Films*., **1995**,269, 117-120.
[19] A.K. Chawla, D. Kaur, R. Chandra, *Opt. Mater.*, **2007**, 29, 995-998 .
[20]. D.D.O. Eya, A.J. Ekpunobi, C.E. Okeke, *Acad. Open Internet J*., **2006**, 17,1.
[21] K. Kurtz, T.T. Perry, *J. Appl. Phys*., **1968**,39, 3798-3814.
[22] P.V. Dhanaraj, N.P. Rajesh, *Physica B.*, **2010**, 405, 4105–4110.
[23] B.W Mott, *Micro indentation Hardness Testing, Butterworth London*, **1956.**
[24] T. Thaila and S. Kumararaman,*Archives of Applied Science Research*, **2012**, 4,3,1494-1501.
[25] E. Meyer, *Z. ver. Dtsch. Ing*, **1908**, 52,645-654.
[26] E.M. Onitsch, *Mikroscopia*, **1947**, 2, 131-151.
[27] M. Hanneman, *Metall. Manchu*. **1941**, 23, 135.
[28] W.A. Wooster, *Physical properties and atomic arrangements in crystals, Reports on Progress in Physics*, **1953,**Vol.16, 62-82.